A Carboxylic Rubber from Polyethylene

This is a preliminary report on preparation and evaluation of the viscoelastic behavior of a new type of carboxylic elastomer obtained in this laboratory. During an exploratory work on development of elastomers from polyethylene and other polyolefins having properties parallel to the well-known sulfochlorinated polyethylene[1] (Hypalon), several labile (high-energy) compounds of carbon, silicon, titanium, phosphorous, sulfur, etc., were introduced during the free-radical chlorination, with a view to anchoring reactive groups on the chlorinated polyethylene backbone so as to provide for its vulcanization/gelation later on. Maleic anhydride, with its high chain transfer and radical scavenging activity[2] gave very promising results. The reaction conditions were simple and flexible, so as to yield readily vulcanizable elastomers of varying chlorine contents and carboxylic groups anchored randomly in desired proportion and spacing. Natural rubber–maleic anhydride grafts,[3] and reclaimed rubber scrap–maleic anhydride compounds[4] are well known. Grafts of maleic anhydride on polyethylene obtained by radical reaction in solution have also been reported.[5] The introduction of carboxyl groups simultaneously with the chlorosulfonyl groups by chlorosulfonation with sulfuryl chloride in the presence of maleic anhydride, has been the subject of an Indian patent.[6] The carboxylic elastomers obtained through copolymerization of butadiene, styrene-butadiene, and butadiene-acrylonitrile with acrylic or methacrylic acids have been studied exhaustively and reviewed.[7] The use of maleic anhydride (and its structural analogs such as chloromaleic anhydride, maleimide, n-phenyl maleimide, etc.) during chlorination opens up a new area of elastomeric materials from hydrocarbon polymers and copolymers. A tentative scheme of the mechanism for such a new combination of free-radical reactions, which may be called chlorocarboxylation, is outlined by some of its major kinetic steps (a detailed kinetic study on dodecane, a model hydrocarbon chain, and the characterization of polymeric species[8] involved in the present study being under way):

1. $Cl_2 + h\nu \rightarrow Cl* + Cl*$ (thermal, photochemical, or peroxide initiation)
2. $P—H + Cl* \rightarrow P* + HCl$ (P—H, polymer, P*, polymeric radical)
3. $P* + Cl_2 \rightarrow P\text{-}Cl + Cl*$ (chlorination)
4. $P* + M \xrightarrow{fast} P\text{-}M*$ [carboxyl grafting with maleic anhydride (M) and its propagation]
5. $P—M* + P \xrightarrow{slow} P—M + P*$
6. $P* + M \xrightarrow{fast} P—H + M*$ (chain transfer)
7. $M* + M* \xrightarrow{fast} M—M$ (dimerization of M)
8. $Cl* + M* \xrightarrow{slow} M—Cl$ (chlorination of M)
9. $M* + n{\cdot}M \xrightarrow{slow} (M)_n - M*$ (homopolymerization of M)
10. $P—M* + P—M* \xrightarrow{fast} P = M + P—M$ (termination by disproportionation)

The kinetic steps 4 and 5 bring about the desired grafting of carboxylic groups, step 3 being the usual radical chlorination of an alkane. Steps 6–9, especially 7, represent the loss of radical concentration (scavenging) by side reactions and explains the marked retardation in the thermal chlorination rates caused by the addition of maleic anhydride. This may be seen from Fig. 1, which shows the percent chlorination versus time of reaction at various concentrations of maleic anhydride. Some results of our exploratory work are given in Table 1. In all the experiments maleic anhydride (or its analog) was added immediately before starting the chlorination by gaseous chlorine, the main reaction, which is purely thermal and sufficiently fast even at 74°C. Maleic anhydride grafting is, however, favored by higher temperatures, as expected.

The carboxyl contents of polymers, expressed as the succinyl group $[C_2H_3—(COOH)_2]$, have been estimated on purified polymers by the nonaqueous alkalimetry and the dye-partition/interaction technique,[9] using a rhodamine dye. All hydrocarbon polymers studied here have undergone substantial carboxylic grafting. Polypropylene, however, is resistant to both chlorination and carboxylic grafting under the experimental conditions. The tensile strength and elongation measurements are based on simple divalent metal oxide cure, namely, elastomer:100, MgO:5 phr, ZnO:5 phr, stearic acid:2 phr; compounded and vulcanized in standard ASTM sheet molds at 150°C for 10 min.
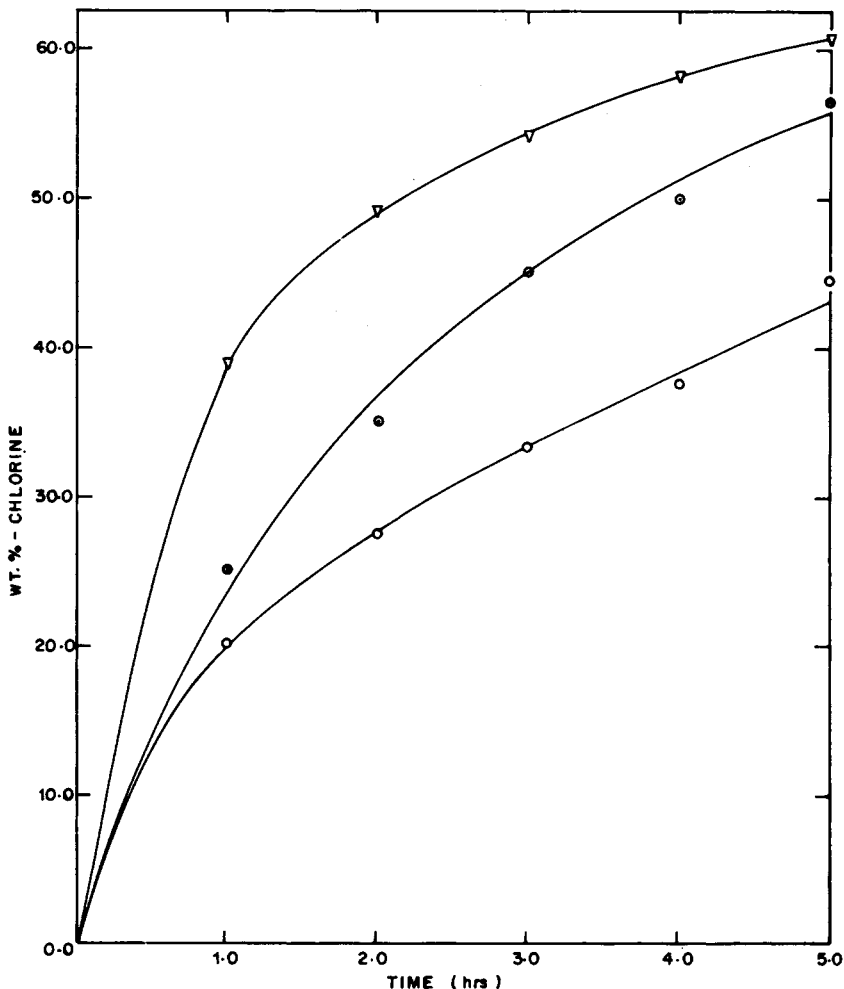
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Fig. 1. Degree of chlorination versus time of free-radical chlorocarboxylation in tetrachloroethane at 110°C. Maleic anhydride: (∇) 0.0 wt. %; ($\odot$) 5.0 wt. %; ($\bigcirc$) 20.0 wt. %.

The chlorocarboxylation thus provides a suitable means of introducing carboxylic groups while subjecting the polymer to ordinary chlorination. Such dual modification of the parent polymer is expected to achieve a unique combination of properties in speciality elastomers, especially adhesion to metal surfaces, higher tensile strength, surface hardness, toughness and tear strength, as well as ozone resistance.

A concomitant advantage of the above method of chlorocarboxylation of polymers is seen from the simplicity with which the treated polymer can be recovered by ordinary steam distillation under partial vacuum. After reaction, the elastomer solution is simply emulsified with excess water and steam distilled. The hydrophillic —COOH groups chemically anchored to the hydrophobic polymer chain provide for sufficient emulsifying action and retention of the polymer in discrete granular/chunk and kettle-dischargable form throughout the operation of solvent recovery. Similar treatment of the sulfochlorinated polyethylene with extraneous surfactants leads to complete hydrolysis of its —SO$_2$Cl groups and results in fast cure cycles and scorching of the product during vulcanization, also impairing its storage life. The chlorocarboxylated polyethylene appears to have almost similar properties to chlorosulfonated polyethylene in many essential features of the speciality elastomer.

TABLE I
Chlorocarboxylation of Hydrocarbon Polymers and Stress-Strain Properties

Exp. No.	Base polymer	Solvent	Period of reaction, hr	Maleic anhydride (charged), %	Temperature, °C	Chlorine content, %	Carboxyl contents as $C_4H_5O_4$	Tensile strength, kg/cm^2	Elongation, %	Remarks
1	Linear HDPE (PIL-Hostalen)	Tetrachloroethane	5	5.0	110	56.4	2.38	120	600	—
2	Linear HDPE (PIL-Hostalen)	Tetrachloroethane	3	20.0	110	32.5	4.05	116	480	—
3	Linear HDPE (PIL-Hostalen)	Tetrachloroethane	5	5.0	90	59.0	0.59	<100	>600 (yields)	—
4	Linear HDPE (PIL-Hostalen)	Tetrachloroethane	3	5.0	110	52.2	2.38	130	500	
5	Branched LDPE (ICI,WRM-19)	Tetrachloroethane	5	5.0 (maleimide)	110	57.1	3.8 $(C_4H_6O_3N)$	92	450	— —
6	Branched LDPE (ICI,WRM-19)	Tetrachloroethane	5	20.0	110	56.2	14.1	—	—	Insoluble and not workable
7	Branched LDPE (ICI,WRM-19)	Carbon tetrachloride	5	20.0	74	59.4	12.7	—	—	Insoluble and not workable
8	Polypropylene (Monticatini)	Tetrachloroethane	5	5.0	110	12.8	0.82	—	—	Not workable
9	Polyisobutylene (Polysar)	Tetrachloroethane	3½	5.0	110	34.4	2.03	—	—	Insufficient sample
10	EPDM rubber (DuPont)	Tetrachloroethane	5	5.0	110	30.4	1.78	—	—	Insufficient sample
11	Poly(cis-1-4-butadiene)	Tetrachloroethane	5	5.0	110	35.0	2.62	—	—	Partial gelation
12	Vinyl polybutadiene	Tetrachloroethane	3½	5.0	110	40.2	1.96	—	—	Gelation
13	Natural rubber	Tetrachloroethane	2	5.0	110	45.3	1.82	—	—	Insufficient sample
14	Nitrile rubber (Chemaprene, 33% AN)	Tetrachloroethane	2½	5.0	110	30.8	2.06	—	—	Insufficient sample

A few structural analogs of maleic anhydride were tried.   Maleimide and substituted maleimides participate with more or less equal vigor in chlorocarboxylation, but introducing monocarboxylic sites, which offer slightly better vulcanizate properties.   A detailed report on these polymer modifications will follow in future publications.   Throughout an exhaustive literature search, only one sketchy reference[10] was found wherein maleic anhydride in excessive quantities was employed to introduce carboxylic sites after prechlorination of polyethylene to 25% chlorine.

References

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